

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
5 February 2004 (05.02.2004)

PCT

(10) International Publication Number
WO 2004/011546 A1

(51) International Patent Classification?: C08L 23/04, 23/08, C08F 297/08

(21) International Application Number: PCT/GB2003/003223

(22) International Filing Date: 29 July 2003 (29.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 0217522.2 29 July 2002 (29.07.2002) GB

(71) Applicant (for all designated States except US): BOREALIS TECHNOLOGY OY [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): MYHRE, Ole, Jan [NO/NO]; Borealis AS, N-3960 Stathelle (NO). SKAR, Merete [NO/NO]; Larer Johnsenvei 2, N-3960 Stathelle (NO). DAVIKNES, Hans, Georg [NO/NO]; Tryms Vei 8, Stathelle (NO). BORVE, Kjetil, Larsen [NO/NO]; Kalliasen 23, Stathelle (NO). JOHANSEN, Geir, Morten [NO/NO]; Borealis AS, N-3960 Stathelle (NO).

(74) Agents: FRANK B. DEHN & CO.; 179 Queen Victoria Street, London EC4V 4JH, (GB).

(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), DE (utility model), DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SCHRINK FILM

(57) Abstract: A shrink film comprising a polyethylene film of thickness 5 to 500 μm , characterized in that said polyethylene comprises an ethylene homopolymer-copolymer mixture having a molecular weight distribution in the range 5 to 40, and a weight average molecular weight of at least 100 kD.

- 2 -

respectively and for a polymer to function adequately as the base material for a shrink film it must meet the different requirements (in terms of melt strength, cold strength and other mechanical properties) of the hot shrink, cold shrink and post-shrinkage stages.

We have now found that these requirements are particularly well met, particularly for relatively thin shrink films, by linear low density polyethylenes (LLDPE) having a high molecular weight distribution (MWD) and containing an ethylene homopolymer and an ethylene copolymer. (The term MWD refers to the ratio (Mw/Mn) between the weight average molecular weight (Mw) and the number average molecular weight (Mn) of a polymer).

Thus, viewed from one aspect the invention provides a shrink film comprising a low density polyethylene film of thickness 5 to 500 μm , e.g. 20 to 120 μm , preferably 30 to 110 μm , especially 40 to 100 μm , characterized in that said low density polyethylene comprises an ethylene homopolymer-copolymer mixture having a molecular weight distribution in the range 5 to 40, preferably 10 to 35, and a weight average molecular weight of greater than 100 kD, e.g. 150 to 300 kD (more preferably 200 to 280 kD, and especially greater than 230, e.g. 230 to 270 kD).

Viewed from another aspect the invention provides the use of a polyethylene composition comprising an ethylene homopolymer-copolymer mixture having a molecular weight distribution in the range 5 to 40, and a weight average molecular weight of at least 100 kD in the manufacture of a shrink film.

In the shrink film of the invention, the homopolymer component preferably has a higher density and lower weight average molecular weight than the copolymer component. Generally, the density of the homopolymer component should be in the range 960 to 980 kg/m^3 while the density of the copolymer should be in the

- 4 -

thickness in the non-shrunk film) varies depending on whether this forms part of a one layer or multilayer structure. However, a preferred thickness is 20 to 200 μm , more preferably 40 to 110 μm , especially when the homopolymer/copolymer mixture layer forms part of a multilayer film. Accordingly, the films of the invention are particularly suitable for wrapping pallets carrying for example up to 1500 kg loads or wrapping relatively small loads, e.g. having a weight per package of 750kg or less, more preferably 50 kg or less. Examples of such loads include magazines, books, bottles, sets of bottles (e.g. with 2 to 12 in a set), etc.

The shrink films of the invention have particularly good properties not just in terms of their performance during the film shrinking operation but also in terms of the mechanical properties of the shrunk film itself. Thus, the shrink film has a particularly beneficial combination of very low hot shrink force and very high cold shrink force. The low hot shrink force serves to reduce hole formation during the shrinking operation (a major problem with conventional shrink films) while the high cold shrink forces provide excellent holding properties, i.e. they serve to stabilize the shrink-wrapped product. Moreover, the shrunk film has mechanical properties (e.g. dart drop and tensile strength) which are improved relative to conventional shrink films, especially at very low temperatures. As a result the shrink films of the invention are especially suited for use in packaging products which will be exposed to low temperatures during transportation or storage. The excellent mechanical properties of the shrunk film are thought to arise at least in part from the fact that the polymer is a homopolymer-copolymer rather than copolymer-copolymer mixture. This combination of properties relevant to shrink wrapping is both unexpected and highly advantageous.

- 6 -

935 kg/m³), a MFR_{2.16} (190°C) of 0.05 to 1.2 g/10 min (e.g. 0.1-0.8 g/10 min), a weight average molecular weight (Mw) of 150000 to 300000 D (preferably 200000 to 280000D, more preferably 230000 to 270000D), and a MWD of 10 to 35 (preferably 15 to 25).

Such a homopolymer-copolymer mixture may be produced according to the technique described in WO 99/41310 using a slurry loop reactor followed by a gas phase reactor, with a density of 931 kg/m³, weight average molecular weight (Mw) of 240000D, MFR_{2.16} (190°C) of 0.2 g/10 min, and an MWD of 22.

In such a two-stage polymerization process, the first stage is preferably an ethylene homopolymerization with the second stage being a copolymerization.

The comonomer used in the copolymer is preferably a C₃₋₁₂ alpha olefin or a mixture of two or more C₃₋₁₂ alpha olefins, e.g. 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene, with 1-butene and 1-hexene being preferred. Hence, the term "copolymer" as used herein is intended to cover terpolymers as well. A preferred terpolymer of use in the invention is an ethylene/butene/hexene terpolymer. The comonomer incorporation in a copolymerization reaction is preferably 2 to 10% mole relative to ethylene, especially 4 to 8% mole.

In the homopolymerization stage, while no comonomer is added it will be appreciated that the ethylene source may contain trace amounts of C₃₊ hydrocarbons copolymerizable with ethylene that may thus become incorporated into the ethylene homopolymer. It is well understood in the industry that the polymer product is nonetheless considered to be an ethylene homopolymer.

For film formation using a polymer mixture it is important that the different polymer components be intimately mixed prior to extrusion and blowing of the film as otherwise there is a risk of inhomogeneities, e.g. gels, appearing in the film. Thus, particularly

- 8 -

production techniques may be used in this regard. Typically the homopolymer-copolymer mixture layer will be extruded through a die at a temperature in the range 160°C to 240°C, and cooled by blowing gas (generally
5 air) at a temperature of 10 to 50°C to provide a frost line height of 2 to 8 times the diameter of the die. To obtain balanced shrink properties, the blow up ratio should generally be relatively high, e.g. in the range 2 to 5.

10 The shrink films of the invention may of course be used to wrap or encase items, e.g. books, magazines, bottles, etc and this forms a further aspect of the invention.

15 Viewed from a further aspect therefore the invention provides a process for wrapping an object comprising applying a shrink film about said object and shrinking said film by the application of heat thereto, characterized in that said film is a shrink film according to the invention.

20 Viewed from a further aspect the invention provides an object shrink wrapped with a shrink film according to the invention.

25 The shrink films of the invention are distinguished from prior art shrink films in their special combination of improved mechanical and shrink properties. During the film forming process a high degree of polymer chain entanglement will occur leading to increased toughness in the shrink film and to a highly oriented structure which provides improved shrinkage properties. Thus the
30 films of the invention exhibit the following advantageous properties: low melt stress (low hot shrink force) reducing hole formation during shrinkage; high cold shrink force, leading to better holding by the shrunk film of objects packaged by it; improved
35 mechanical properties for the shrink film, allowing more demanding (e.g. sharp edged) products to be shrink wrapped and/or allowing thinner films to be used (and

- 10 -

shrink films formed using the homopolymer-copolymer mixture may be used for shrink wrapping both small and large objects and collections of objects. Thus viewed from a further aspect the invention provides a unilamellar polyethylene shrink film, characterized in that said polyethylene comprises an ethylene homopolymer-copolymer mixture having a molecular weight distribution in the range 5 to 40, and a weight average molecular weight of at least 100 kD (more preferably 200 to 280 kD, and especially 230 to 270 kD). Such films may typically have thicknesses of from 5 to 500 μm e.g. 100 to 200 μm .

The invention will now be described further with reference to the following non-limiting Examples.

Various terms and properties referred to herein are defined or determined as follows:

Molecular Weight Distribution (MWD): This is defined as M_w/M_n where M_w is the weight average molecular weight (in Daltons) and M_n is the number average molecular weight (in Daltons). These are determined by gel permeation chromatography.

$MFR_{2.16}$ and $MFR_{21.6}$ are melt flow rates determined at 190°C according to ISO 1133.

Density is determined according to ISO 1183.

The hot and cold shrink forces have been measured in both Machine (MD) and Transverse (TD) directions in the following way. Specimens of 15mm width and 200mm length are cut out from the film sample in both MD and TD. The samples are tightly mounted into the jaws of the tensile cell in such a way that the distance between the jaws is 100mm and the actual force is zero. The samples are then exposed to hot air at 250°C in a closed chamber for 1 minute while the forces are measured. The maximum force is recorded represents the hot shrink force. The hot air chamber is removed while continuing to record the tensile force. The maximum force is again recorded and this second maximum represents the cold shrink

- 12 -

Impact resistance (determined on Dart-drop (g/50%))

Dart-drop is measured using ISO 7765-1, method "A". A dart with a 38 mm diameter hemispherical head is dropped from a height of 0.66 m onto a film clamped over a hole.

If the specimen fails, the weight of the dart is reduced and if it does not fail the weight is increased. At least 20 specimens are tested. The weight resulting in failure of 50% of the specimens is calculated.

Puncture resistance (determined in Ball puncture (energy/J) at +23°C, -20°C and -40°C)

The method is according to ASTM D 5748. Puncture properties (resistance, energy to break, penetration distance) are determined by the resistance of film to the penetration of a probe (19 mm diameter) at a given speed (250mm/min).

Tear resistance (determined as Elmendorf tear (N))

The tear strength is measured using the ISO 6383 method.

The force required to propagate tearing across a film specimen is measured using a pendulum device. The pendulum swings under gravity through an arc, tearing the specimen from pre-cut slit. The specimen is fixed on one side by the pendulum and on the other side by a stationary clamp. The tear strength is the force required to tear the specimen.

Film thickness profile (2-Sigma/%)

In the laboratory the film thickness profile is measured by a non-touchable (capacitive) measuring (sensor) system from Octagon Process Technology. From this measurement one can also get average thickness, min./max. thickness, standard deviation and calculated tolerances expressed as 2-Sigma.

Outside and inside friction (cof)

Friction is measured according to ISO 8295. By

Table 1

	Film 1	Film 2	Film 3*
Film thickness [μm]	150	150	150
Extrusion temperature [$^{\circ}\text{C}$]	200	200	200
Blow Up Ratio (BUR) [1:x]	3	3	3
Frost Line Height (FLH) [mm]	900	900	900
1% Sec. modulus MD [MPa]	160	160	300
1% Sec. modulus TD [MPa]	170	160	330
Free shrinkage at 160 $^{\circ}\text{C}$ MD [%]	67	64	46
Free shrinkage at 160 $^{\circ}\text{C}$ TD [%]	38	30	20
Hot shrink force MD [g]	19	11	5
Hot shrink force TD [g]	5	2	1
Cold shrink force MD [g]	340	320	500
Cold shrink force TD [g]	300	330	500
Dart Drop Index [g/50%]	590	640	950
Tear resistance MD [N]	3.4	8.5	20

* of the invention

Example 2Shrink Films

Two shrink films of 115 μm thickness were prepared by blown film extrusion as co-extruded films with a conventional film extruder. The co-extrusion line was equipped with three extruders and a die having a die diameter of 200 mm and die gap of 1.0 mm. The film blowing took place at an extrusion temperature of 200 $^{\circ}\text{C}$ with a blow up ratio of 1:3.8 and frost line height of 900 mm.

Film 4 was prepared with all three layers being of the same material as Film 1. Film 5 was prepared with the outer layers being of the same material as Film 1 and

- 16 -

900 mm.

Film 6 was produced with the same material in all layers, namely a LDPE with $MFR_{2.16}$ (190°C) 0.7 g/10 min and density 927 kg/m³ manufactured using a tubular high pressure process.

Film 7 was produced with the surface layers being of the same material as film 6 while the core layer was produced with the material used for Film 3. The layer distribution of this film was 25/50/25% (w/w/w).

Film 8 was produced with the same material in all layers, namely the material used for Film 3.

The shrinkage and mechanical properties of the three films were measured and the results are listed in Table 3 below.

- 18 -

Claims

1. A shrink film comprising a polyethylene film of thickness 5 to 500 μm , characterized in that said
5 polyethylene comprises an ethylene homopolymer-copolymer mixture having a molecular weight distribution in the range 5 to 40, and a weight average molecular weight of at least 100 kD.
- 10 2. A shrink film as claimed in claim 1 wherein the homopolymer has a density of 960 to 980 kg/m^3 .
3. A shrink film as claimed in claim 1 or 2 wherein the copolymer has a density of 890 to 920 kg/m^3 .
- 15 4. A shrink film as claimed in any one of claims 1 to 3 wherein the density of the homopolymer-copolymer mixture is 920 to 945 kg/m^3 .
- 20 5. A shrink film as claimed in any one of claims 1 to 4 wherein the Mw of the homopolymer-copolymer mixture is 150 to 300 kD.
- 25 6. A shrink film as claimed in any one of claims 1 to 4 wherein the Mw of the homopolymer-copolymer mixture is at least 230 kD.
- 30 7. A shrink film as claimed in any one of claims 1 to 6 wherein the MWD of the homopolymer-copolymer mixture is in the range 10 to 35.
8. A shrink film as claimed in claim 7 wherein the MWD of the homopolymer-copolymer mixture is in the range 15 to 25.
- 35 9. A shrink film as claimed in any one of claims 1 to 8 wherein the ratio of homopolymer to copolymer in said

- 20 -

said film by the application of heat thereto, characterized in that said film is a shrink film according to any one of claims 1 to 18.

5 20. An object shrink wrapped with a shrink film according to any one of claims 1 to 18.

21. Use of a polyethylene composition comprising an ethylene homopolymer-copolymer mixture having a
10 molecular weight distribution in the range 10 to 35, and a weight average molecular weight of at least 150 kD in the manufacture of a shrink film.

22. A polyolefin shrink film having a Dart drop value
15 (g)/film thickness (μm) of 5 g/ μm or more.

23. The shrink film of claim 22 comprising an ethylene homopolymer/copolymer mixture.

20 24. The shrink film of claim 22 or 23 wherein the film is unilamellar.

25 25. The shrink film of claim 22 to 24 wherein Dart drop value (g)/film thickness (μm) is 6 g/ μm or more.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/GB 03/03223

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9903902	A	28-01-1999	AT 223445 T 15-09-2002
			AU 744972 B2 07-03-2002
			AU 8286298 A 10-02-1999
			BR 9810771 A 30-10-2001
			CN 1265119 T 30-08-2000
			DE 69807702 D1 10-10-2002
			DE 69807702 T2 02-01-2003
			EP 0996651 A1 03-05-2000
			ES 2178232 T3 16-12-2002
			JP 2001512147 T 21-08-2001
			NO 20000279 A 20-03-2000
			PL 338511 A1 06-11-2000
			TR 200000180 T2 21-06-2000
			WO 9903902 A1 28-01-1999
			US 6319989 B1 20-11-2001
			US 6451916 B1 17-09-2002
			ZA 9806434 A 20-01-2000
			HU 0003291 A2 28-12-2000
EP 0404368	A	27-12-1990	EP 0404368 A2 27-12-1990
			PT 94246 A 08-02-1991
GB 2097324	A	03-11-1982	BE 892927 A1 22-10-1982
			CA 1174423 A1 18-09-1984
			DE 3215120 A1 09-12-1982
			FR 2504537 A1 29-10-1982
			IT 1151736 B 24-12-1986
			JP 1688905 C 11-08-1992
			JP 3054048 B 19-08-1991
			JP 57181828 A 09-11-1982
			NL 8201675 A ,C 16-11-1982
			US 4597920 A 01-07-1986